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Review Article

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Carbon nanostructured as cathode materials for lithium-sulfur batteries with improved electrochemical

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ABSTRACT

Remarkable progress has been made in developing high performance lithium-sulfur batteries, especially in the development cathodes with high energy densities. In this view, the key points for the development of excellent lithium-sulfur batteries cathodes are highlighted in the following areas: sulfur-containing nanotubes/nanofibers, graphene-sulfur electrodes and porous carbon sulfur composites. In addition, the current challenges in this field for practical applications of lithium-sulfur batteries are further discussed.

Key words: cathode materials, lithium-sulfur batteries, cycling stability, energy storage.

INTRODUCTION

In the last decades, rechargeable lithium batteries have become incredibly popular energy storage devices for applications in portable equipment, such as mobile phones, notebook computers, and even electric vehicles, due to their proven track record and decent battery performance[1-4]. Rechargeable lithium batteries are considered as the key technology in the dissemination of electromobility[5]. However, along with the continuous development of technology and progress of industry, lithium batteries still face many challenges. Electronic devices are being developed to be more portable, thinner, smaller, and longer lasting. This trend has spurred intense research into developing electrodes which are thinner but that have higher capacity densities.

Lithium-sulfur batteries are believed to be one of the most promising energy storage systems for electric vehicles due to their high theoretical specific capacities (1675 mAh g-1) and energy density(2600 Wh kg-1)[6]. Sulfur is abundant, low-cost and environmentally friendly, which makes it extremely beneficial for high-energy density devices.

However, compared with more common lithium-ion batteries, several critical problems hinder the wide-scale commercial use of lithium-sulfur systems. In attempts to overcome the above drawbacks, large quantities of strategies have been explored, such as research on electrodes, electrolytes, additives, binders, and separators[7-9].

This short review article summarizes the recent advances in lithium-sulfur batteries of sulfur cathodes. Many pioneering research studies have been conducted to look into combining sulfur with conductive materials such as nanotubes/nanofibers, graphene-sulfur electrodes and porous carbon sulfur composites[10].

Sulfur-containing nanotubes/nanofibers

A wide variety of synthetic approaches for the nanostructuring and the benefits obtained from the nanostructuring are introduced[11-12]. Scientist fabricated carbon nanofibers[13-15] and carbon nanotubes[16-20]as lithium-sulfur batteries[21]. To obtain high electronic conductivity and prevent dissolution of polysulfides into the electrolytes, in Han et al ‘s work, they designed and prepared multi-walled carbon nanotubes (MWCNTs) by using thermal chemical vapor deposition, which was to be an inertia additive material for elemental sulfur active electrodes for lithium-sulfur batteries[22]. Moreover, the volume expansion of sulfur during cycle can be accommodated by the flexible carbon nanotubes[23].

The sulfur/MWCNT composite was manufactured by Ahn et al, which acted as the cathode material for lithium-sulfur batteries[24]. In order to investigate the extensively effect of sulfur/MWCNT, its structural and electrochemical properties were characterized broadly. However, they found that was not trapped strongly to the nanotubes and it dissolved quickly. As a consequence, the discharge capacity was measured to be low up 30 cycles[24]. Amazingly, S-coated-MWCNT (sulfur-coated multi-walled carbon nanotubes composite material has recently been achieved by Yuan et al Derived from their studies, S-coated-MWCNT should be an excellent material as cathode[25]. Despite of those remarkable advance achieved recently in S-coated-MWCNT performance, it still faced some key challenges[24]. For example they observed a low initial capacity with only 650 mAh g-1,which is unbelievable that sulfur was strictly coated on the S-coated-MWCNT[23].

To solve this problem, Zheng et al[26] had come up that a empty carbon nanofiber-encapsulated cathode for effective trapping of polysulfide[27-28]. They also attempted to prove high specific capacity and wonderful electrochemical cycle of cells. They achieved the empty carbon nanofiber arrays by using anodic aluminum oxide (AAO) templates, with the atmosphere of thermal carbonization of polystyrene[26]. The AAO not only prevents sulfur from coating onto the exterior carbon wall but also make sulfur infusion into the empty carbonfiber. The high aspect ratio of the carbon nanofibers makes sure a good place for trapping polysulfide, as well as the thin carbon wall makes rapid transportation of lithium ions[26]. More over, it reduced the mastication of electrode materials due to volume expansion[26]. Figure 1 shows that the schematic of design and manufacture process of empty carbon nanofiber/sulfur composite structure[29].

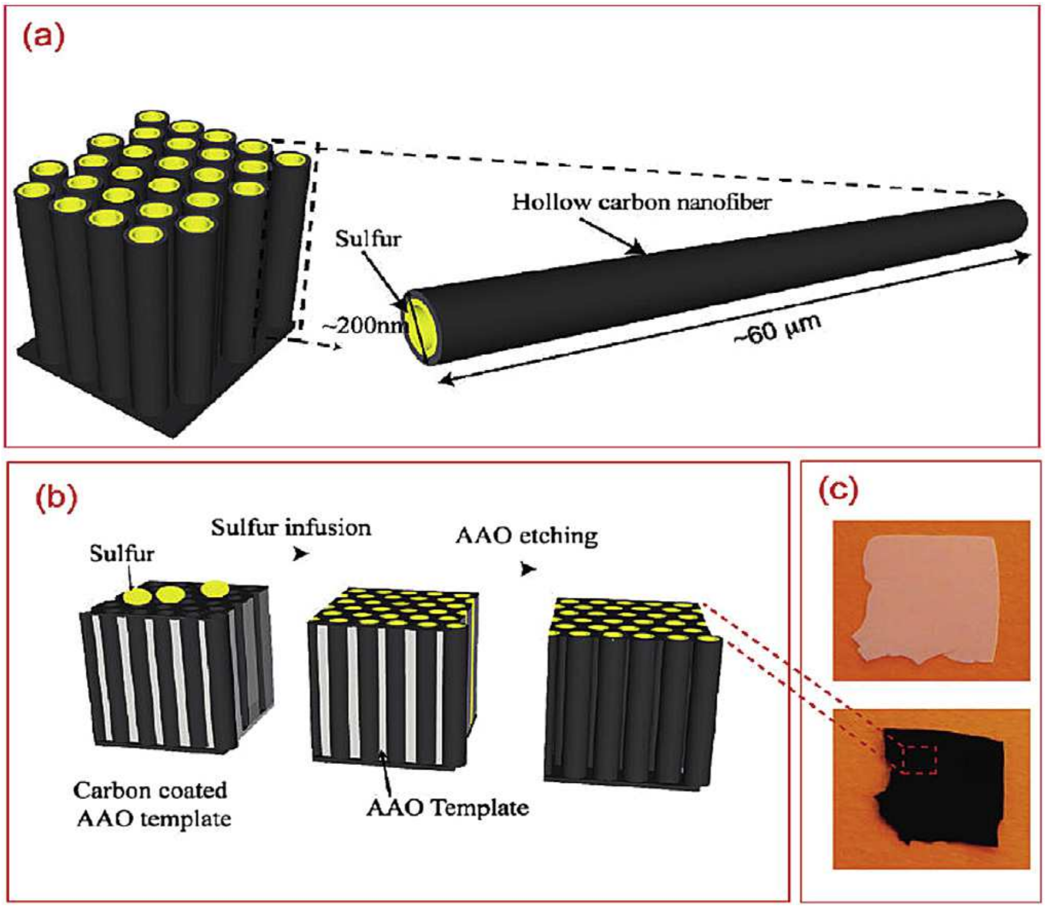

Fig. 1. Schematic of design and fabrication process of hollow carbon nanofiber/sulfur composite structure. (a) The design principle showing the high aspect ratio of the hollow carbon nanofibers for effective trapping of polysulfides, (b) the fabrication process of carbon/sulfur cathode structure, and (c) digital camera images showing the contrast of the AAO template before and after carbon coating and sulfur infusion. Reproduced from Ref. [30] with permission of American Chemical Society

Grapheneesulfur electrodes

Significant advances in graphene sheet-sulfur (FGSS) are opening the door for cathode material for lithium-sulfur batteries. Nevertheless, it is not widely investigated as the host sulfur in the cathode because of its sheet-like shape and opening structure, which caused positive materials to readily diffuse out[31-33]. Some researches have showed promising results. Zhou et al invented a sandwich shape which was designed with pure sulfur between two graphene membrances[34]. The graphene membrances enhanced the rate and cycle performance of lithium-sulfur batteries. Moreover, the other coating separator provides a strong barrier layer to prevent the diffusion of polysulfide to the anode[35]. Similarly, X. Wang et al reported a structure that employs a reduced graphene oxide film between the cathode and the separator shows great potential for capacity too[36].

Differed from above, another effective derivatization approach was to produce a precision manufacturing to strict sulfur when it provided perfect ionic and electronic conductivity. Wang et al preferred to engineer a graphene-sulfur composite material through a special method of wrapping polyethylene glycol (PEG) coated submicrometer sulfur particles with lightly oxidized graphene oxide sheets[37], which were decorated by carbon black nanoparticles(Figure 2)[38]. Rational design for PEG and graphene coating layers were significant to accommodating volume expansion, coated sulfur points during discharge, trapping soluble polysulfide intermediates The graphene-sulfur composite showed that it is a promising cathode material for lithium-sulfur batteries with high energy density[38].

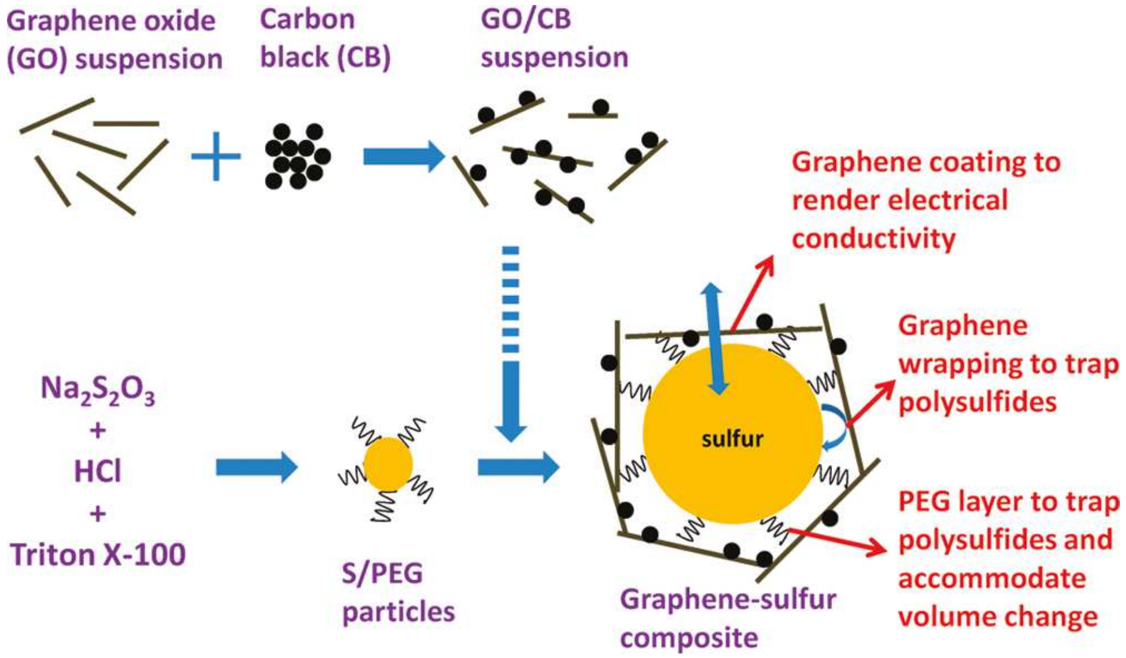

Fig 2.Schematic of the synthesis steps for a graphene sulfur composite, with a proposed schematic structure of the composite

Porous carbon sulfur composites

Undoubtedly, plants use their stems and organisms to protect cell walls as well as make channels for water uptake[39]. In fact, porous structures play an important role in it. So some of them can b used to make hard porous materials[40]. Porous structures are commonly seen in nature, but they are expensive or hard to get materials with porosity, especially with hiererchical ordered porosity (Figure 3). Thanks to Stein et al[41-42], he has published articles emphasizing on how porous materials are synthesised for applications in lithium-sulfur batteries. It is effective ways for synthesise of goal porous materials with hard and soft templating.

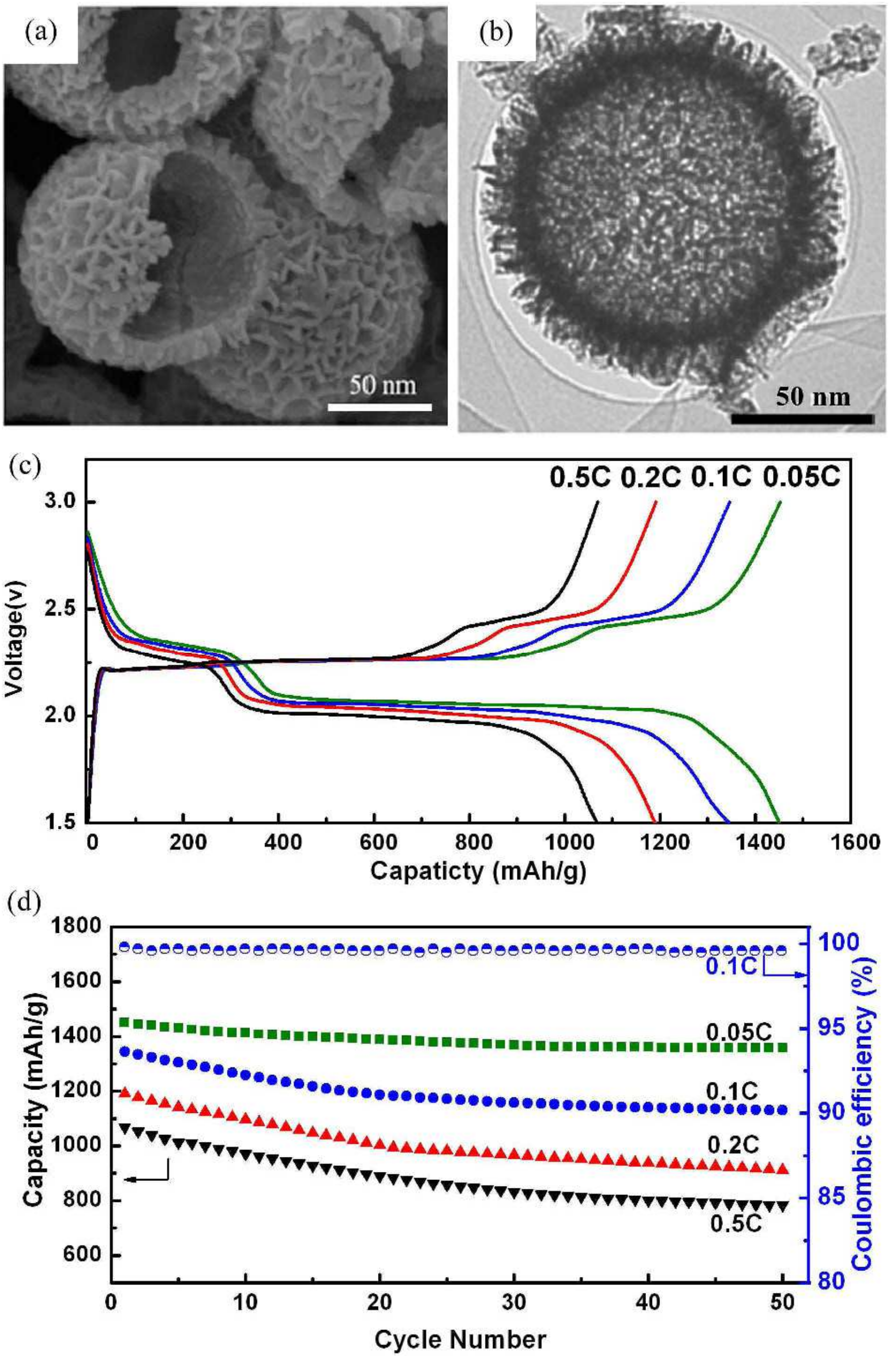

Figure 5. SEM (a), TEM (b), discharge and charge curves (c), and cycling performance (d) of carbon-sulfur composite [43]. Copyright 2013, Springer-Link

CONCLUSION

S-coated-MWCNT is shown to enhance the electrical conductivity and structural stability of composite.The improvement of PEG helps to stabilize the structures of the sulfur cathode during discharge. Hierarchy in pore sizes play a vital role in the electrolyte through a porous electrode, which can be used as potential cathode materials of Li-S batteries. To obtain the more efficient lithium-sulfur batteries, there are still a lot of challenge in this field.

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